



Environmental Solutions

Klozur® CR

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Combined Chemical and Bio-Remediation

Klozur® CR

A combination mixture that supports a two fold mechanism for treating contaminates of concern, short term In Situ Chemical Oxidation (ISCO), with alkaline activated Klozur® persulfate and an electron acceptors for longer term biological oxidation, via PermeOx™ Plus.

- One package treatment for ISCO and Bio-remediation
- Self activating system

Oxidation – Reduction Potentials of Various Chemistries

		<u>volts</u>	
	HF	3.0	↑ stronger oxidizer
	OH•	2.7	
	SO ₄ •	2.6	
	O ₃	2.4	
	S ₂ O ₈ ⁻²	2.1	
	H ₂ O ₂	1.8	
	MnO ₄ ⁻	1.7	
	HClO	1.6	
	Cl ₂	1.4	
	ClO ₂	1.3	
	ClO ₄ ⁻	1.4	

Treats wide range of contaminants
Short subsurface lifetime
Potential for mis-handling

Treats wide range of contaminants
Short subsurface lifetime
Limited use in saturated zone

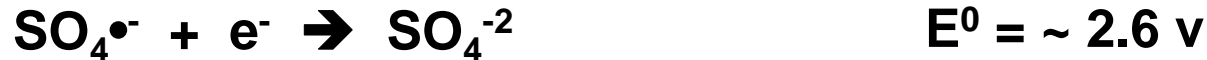
Treats limited range of contaminants
Long subsurface lifetime
Potential effects on hydrogeology

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But, in general, direct oxidation by persulfate anion is *kinetically slow.....*

need to activate

Sulfate free radical:



- very strong oxidizer and kinetically fast
- free radical chemistry is not necessarily straightforward or stoichiometric

The key is how to activate persulfate for your contaminant and site conditions!

Klozur™ Persulfate Activation Chemistries

Conventional

- heat
- divalent metals (Fe^{+2})

FMC Klozur™ Chemistries (patent pending)

- chelated metals
- hydrogen peroxide activation
- **Alkaline pH**

One key to success: Proper activation for your contaminant and site lithology and hydrogeology

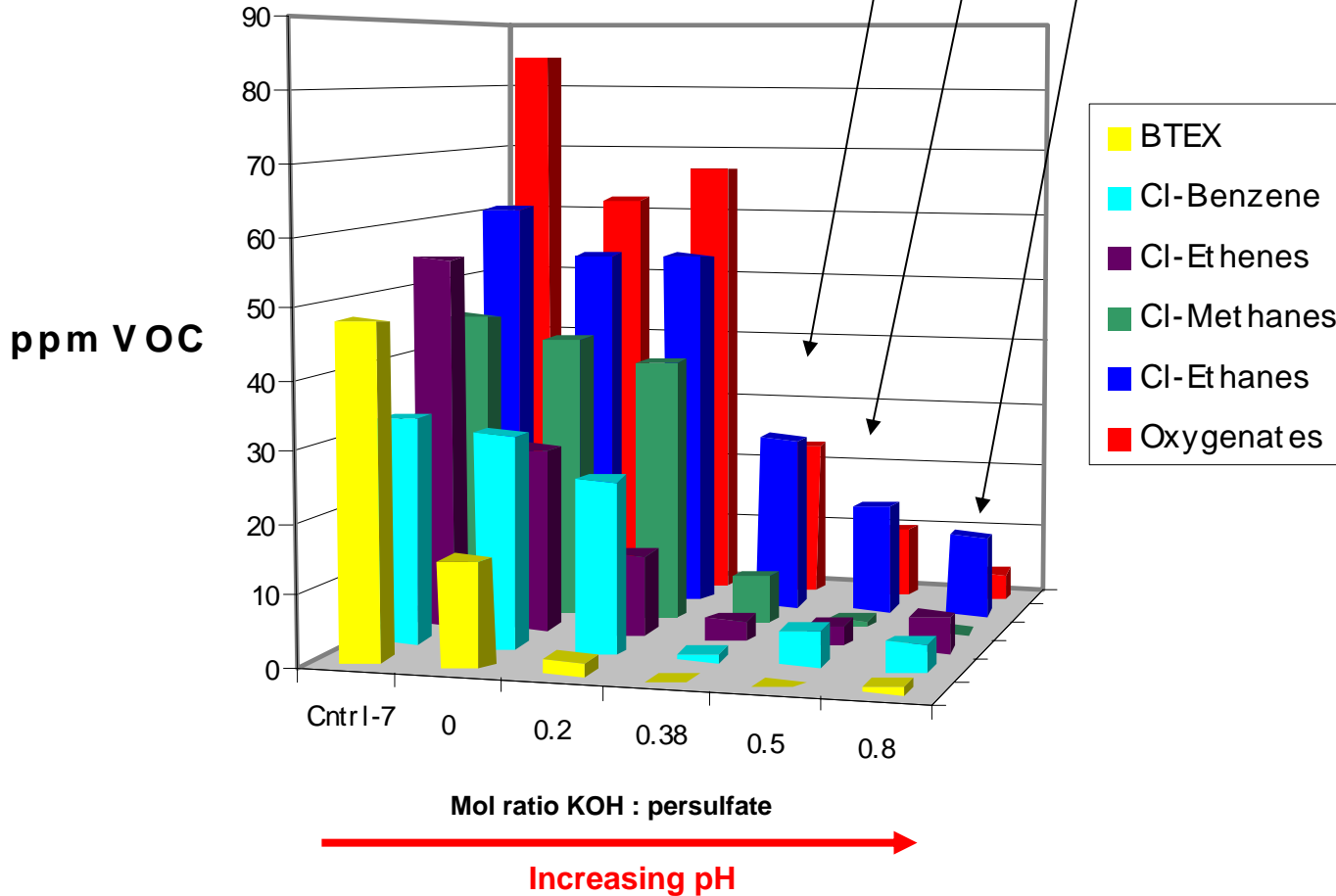
pH 10, pH 1, pH12

Klozur™ Activation Chemistries

Alkaline Activation

- pH > 10

Degradation of COC Utilizing Alkaline Activation



Treatability Study

Room temperature
 Aqueous solutions
 25 g/L sodium persulfate
 KOH as pH modifier
 7 days
 Analyzed by GC-MS

PermeOx® Plus

Use:

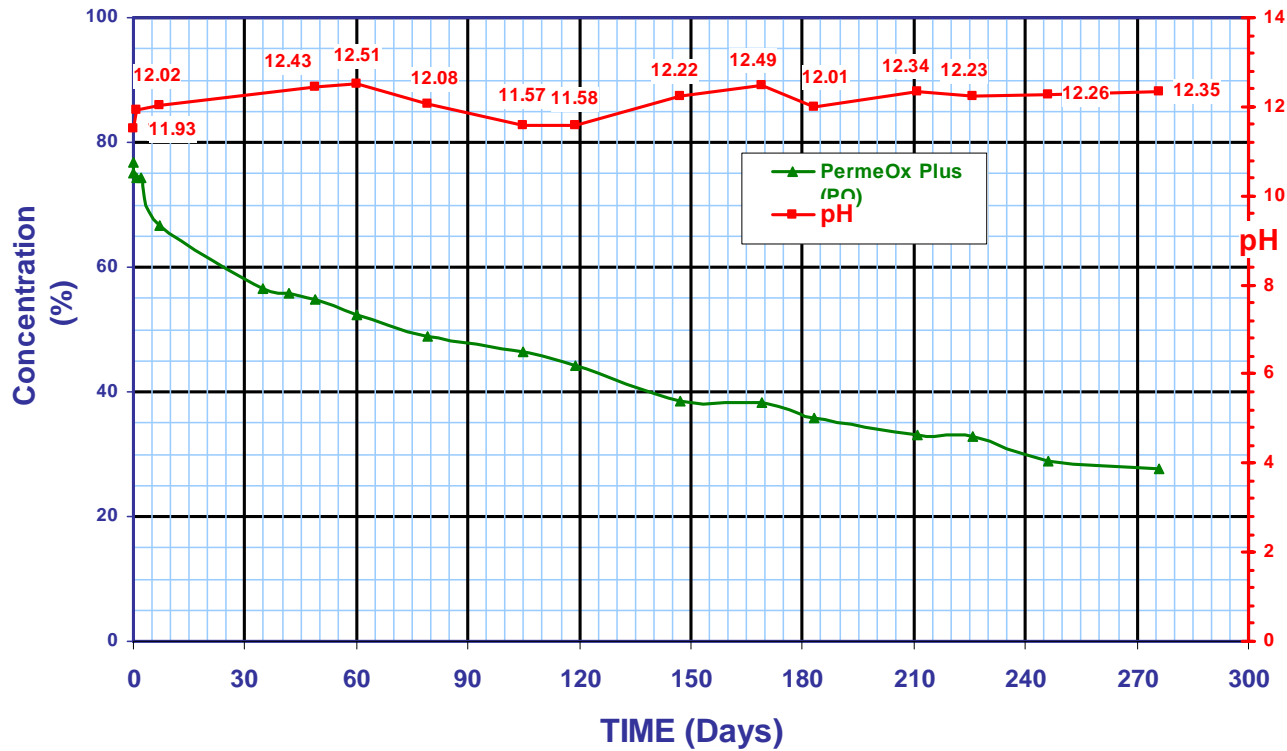
Bio-remediation of Chemicals of Concern
Natural Attenuation is often limited by the amount of oxygen available to the microbiological population

PermeOx® Plus provides slow release of oxygen for enhanced natural attenuation

Examples

- Petroleum Hydrocarbons Remediation
- Creosote Remediation

Fig. 1: Hydrolysis of PermeOx Plus in DI Water at 25°C



Chemistry

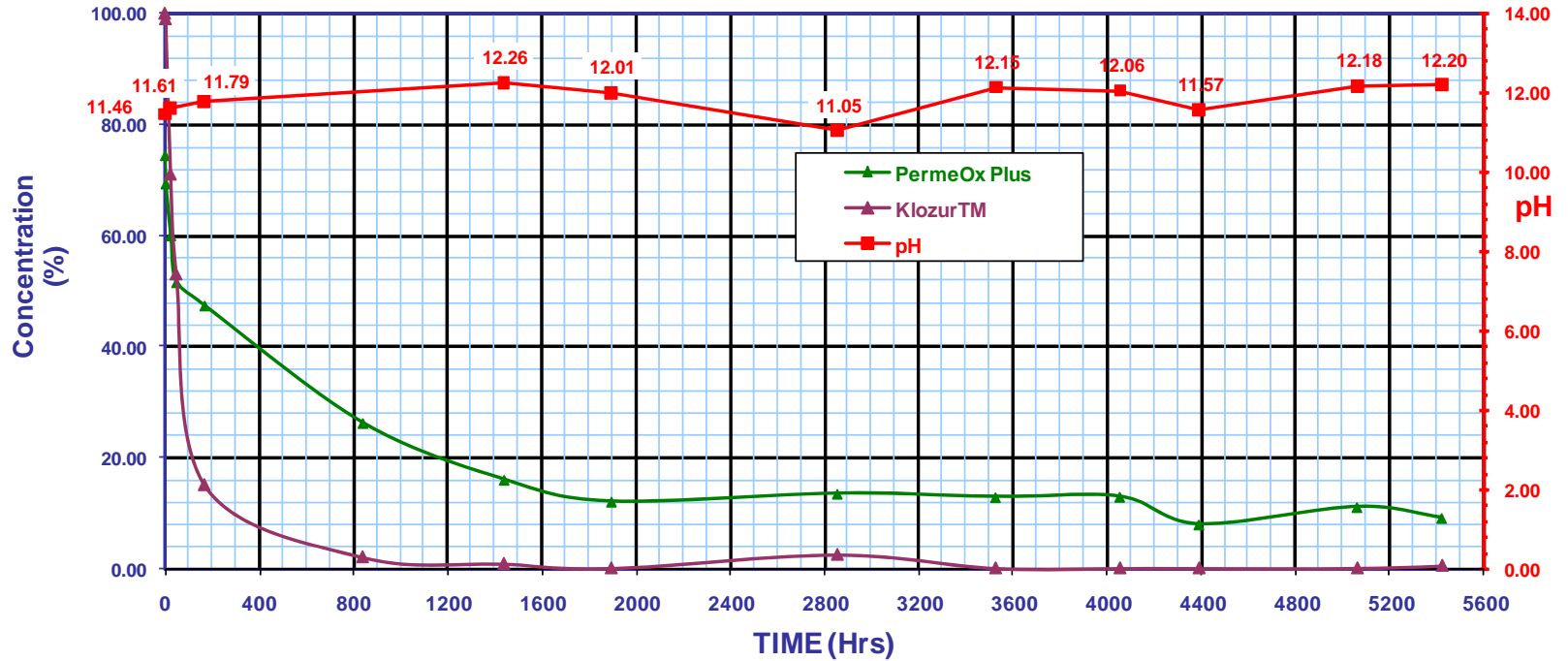
- Coupled Chemical Oxidation and Bioremediation
- $S_2O_8^{=}$ + Activator \rightarrow $2SO_4^{*-}$
- CaO_2 (engineered) + $H_2O \rightarrow Ca(OH)_2 + H_2O_2$
- $2H_2O_2 \rightarrow O_2 + H_2O$

Characteristics of Klozur CR

pH above 10 for life time of Klozur Persulfate

Sufficient Oxygen Release for more than 180 days

Fig. 4: Hydrolysis of PermeOx Plus/Klozur™ in DI Water at 25°C





Acknowledgement

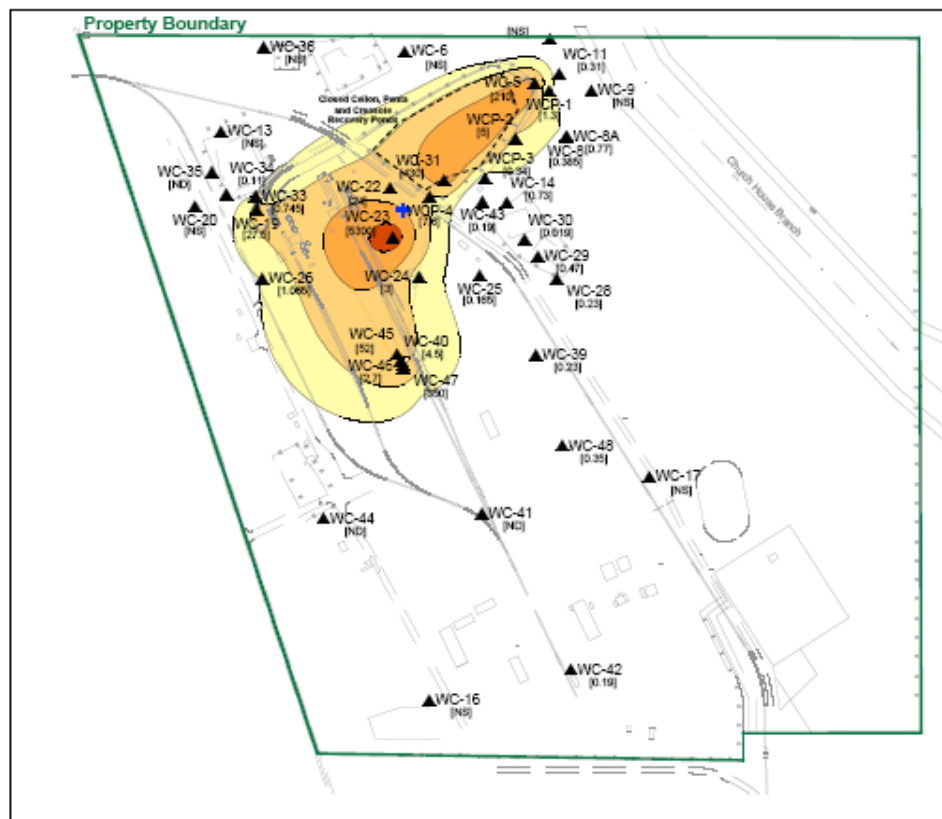
Environmental Solutions

- Innovative Coupled Chem-Bio Treatability Study leading to Large Scale Pilot Test at a Wood Treating Facility
- James Studer, Michael Lee, Ph.D, Jack Sheldon, Norm Kennel

- Lab Study *
- 1225 Acre active wood treating facility in Mississippi
- Semi volatile organic compounds (SVOC)
 - Pentachlorophenol (PCP), Naphthalene, Anthracene Benzo(a)anthracene, Benzo(a)pyrene, Pyrene, et. al

- Geochemical data
- Thick sequence of alluvium
- Contaminant loading as high as 3400 mg/Kg TOC, 448 mg/Kg COD
- Soil/Groundwater
- pH 3.8 – 4.3
- ORP -38 to 24 mV

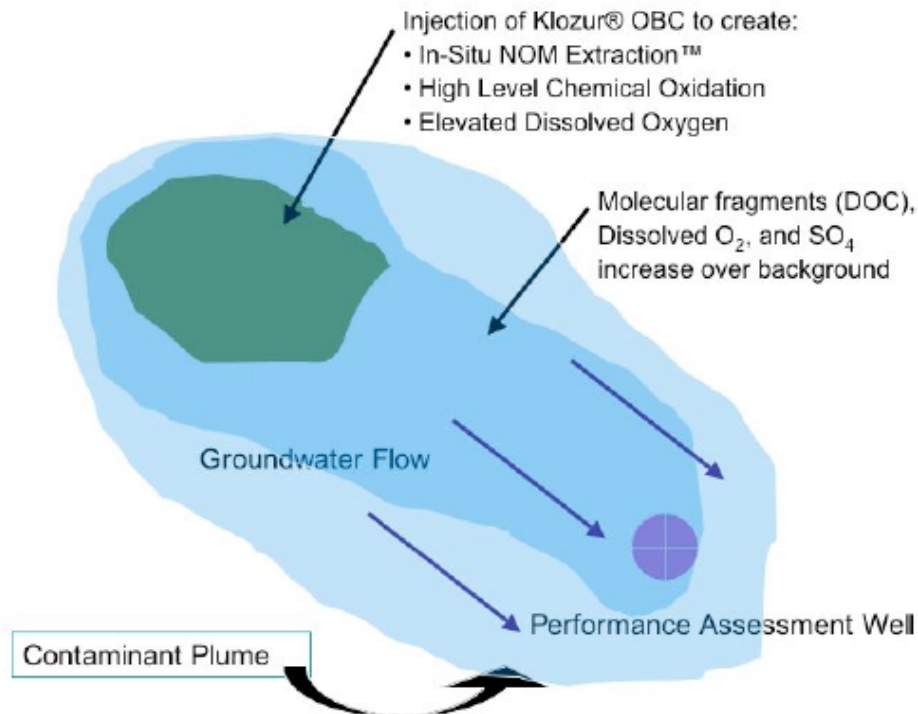
Figure 1. Site Plan – Active Operations Area with PCP Plume as of 2006



- Treatment Strategy
 - Coupled oxidative and bio-remediation
 - Hot spots WC 5 and WC23
 - Enhance bio treatment WC 40

 - Alkaline Activated Klozur Persulfate for rapid and complete chemical oxidation
 - Long term oxygen supply from PermeOx Plus to sustain aerobic biodegradation

Figure 3. Conceptualization of Coupled Chemical Oxidation - Oxidative Biodegradation



- Treatability Study Design
- Initial Conditions
 - Soil
 - 3400 mg/kg TOC 440 mg/kg COD
 - ORP -38 mv
 - pH 3.8
 - 1.5 PPM PCP, 120 PPM Naphthalene, 13 PPM Anthracene, 1.0 PPM Acenaphthylene, 8.6 PPM benzo(a)anthracene, 0.36 PPM 2,4 dimethylphenol, 37 PPM pyrene
 - Ground water
 - 46 mg/L COD
 - ORP 24 mV
 - pH 4.3
 - 4.9 PPM PCP, 0.6 PPM 2,4,6 trichlorophenol

- Destruction Removal Efficiency (DRE)
 - Long term test to investigate the effectiveness of Klozur CR to destroy soil and ground water contaminants

- Analyses performed on the following sample

		<u>pH</u>	<u>ORP</u>	<u>DO</u>
•Time 0	no treatment	4.3	257mV	8.6 mg/l
•Day 1	~20.2 g/kg	10.4	70 mV	8.3 mg/l
•Day 8	~3.23 g/kg	8.3 (adj pH 11)	163mV	9.5 mg/l
•Day 29	~3.23 g/kg	7.3 (adj pH 11)	182 mV	9.4 mg/l
•Day 64	~1.67 g/kg	8.8	124 mV	7.4 mg/l

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- DRE Test
 - Initial Concentration (10-100 PPM)
 - Naphthalene, anthracene, pyrene benzo(a)anthracene
 - 64 day anthracene, non detect
 - Others > 50% reduction
- DRE Test
 - Initial Concentration (< 10 PPM)
 - PCP, benzo(a)pyrene
 - 64 day benzo(a)pyrene non detect
 - PCP non detect
 - All other reduced by > 50%
- ISCO is an effective method to destroy aromatic compound and chlorinate aromatic compounds

Environmental Solutions

- Biologicals

- Initially

2.08X10⁷

- Proteobacteria 48%
 - Firmicutes 26%
 - General bacteria 10.2%
 - Anaerobic bacteria remainder

- 29 day results

2.2X10⁶

Anaerobes reduced as soil became more aerobic
General bacteria increased

- >64 day

6.7X10⁶

Proteobacteria increased

- Conclusion

- No sterilization of the soil
 - Slight reduction of microbial population that rebounded
 - Change to more aerobic microbial population
 - No organisms detected with slowed growth or reduced permeability

- Preliminary Field Results (5 months)
- pH > 10
- Dissolved oxygen significantly increased
- ORP significantly increased
- COC's reduced by as much as 50%